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**Project Title:** Catalytic and Transport Mechanisms of Supercritical Fuels

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## 1.000 Summary

The research on "*Catalytic and Transport Mechanisms of Supercritical Fuels*" is directed towards an understanding of the fundamental science involved in the stabilization of a commercial cracking catalyst, when a hydrocarbon feed under supercritical conditions is cracked into products. The following is a summary of the results that were obtained within the scope of the research program, describing novel technologies in supercritical fluid science, catalysis and *in situ* reaction monitoring. Details of this research may be found in our Annual Report to the AFOSR dated September 1, 1996.

[1] Catalytic cracking studies on a model hydrocarbon, n-heptane, under supercritical heptane conditions in a variety of nanoporous zeolite catalysts demonstrated that the cracking catalyst could be stabilized for many hours when operated under supercritical conditions. Under typical commercial reaction conditions, the catalyst deactivates within seconds.

[2] This research developed the first spectroscopic technique available for general laboratory research to examine the surface chemistries of both porous and non-porous materials under conditions of both high temperatures and pressures. The most forcing conditions tested over long periods of time were 75 atm and 500°C, and the method which we developed in our laboratory is based on Cylindrical Internal Reflection Infrared Spectroscopy (CIR-FTIR). Our inspection of the literature shows that this technique is more powerful and far more available than the EXAFS and EELS methods for *in situ* analysis of the chemistry of the solid surfaces.

[3] Our supercritical fuels work using the CIR-FTIR technique enabled one to examine the *in situ* chemistry of both the internal and external catalyst surface acidic groups, while the on-line gas chromatographic analysis monitored the detailed conversion and product selectivities. Using this coupled technique, the detailed mechanism of hydrocarbon catalytic cracking and catalyst stabilization under supercritical fluid conditions could be elucidated for the first time.

[4] The ramification of the *in situ* reaction monitoring results is that it is the first case in the literature to describe a technique for the high temperature and high pressure analysis of surface

chemistries, and now is generally available for the mechanistic analysis of many catalytic reactions under autogenous reaction conditions.

[5] A surprising result is the observation for the first time that when microporous materials are exposed to a fluid under supercritical conditions, the fluid thermodynamics is altered due to the pore to afford fluid densities even at high temperatures of 500°C which are slightly greater than the fluid densities at room temperature. This phenomenon was demonstrated within the pores of several zeolites of radically different pore sizes and structures. The observation of super-dense phases is important for the stabilization of fuel conversion catalysts under high conversion, supercritical conditions, and it suggests a wide variety of chemical processes may be greatly facilitated by carrying out these reactions in the supercritical regime within microporous materials where super-concentrated reactant species are observed.

[6] The experiments performed to simulate coke solubilization by supercritical fluids using the CIR-FTIR technique in well stirred autoclaves showed a surprising alkylation reaction between the supercritical hydrocarbon solvents (i.e. propane, butane, butene, etc.) and aromatic hydrocarbon solutes (i.e. phenanthrene, 2,3-benzanthracene). The infrared analysis also showed that the substituted aromatic hydrocarbon product and the unreacted aromatic solute were effectively solubilized by the supercritical solvent. The reaction efficiency depended on the nature of the C-H bond interacting with the aromatic solute, and the steric constraints of the hydrocarbon molecule.

[7] The CIR-FTIR technique was also successfully used for the determination of the transport properties (i.e. diffusivities) of hydrocarbons in porous catalysts at high temperatures and pressures. This was the first time that the intracrystalline diffusivity of hydrocarbons in microporous media could be determined under supercritical conditions by using a dynamic technique. The diffusion time constants obtained for single and binary systems proved a liquid like behavior of the hydrocarbon within the zeolite micropores under supercritical conditions in complete agreement with the *in situ* reaction studies. These results are exceptionally important to industrial researchers involved in new process and catalyst development.

## 2.000 Introduction

One of the largest scale catalytic processes practiced in the petroleum industry is the cracking large petroleum molecules into smaller hydrocarbons, primarily in the gasoline range. In the United States, cracking capacity exceeds 10-15 million barrels per day. However, the efficient conversion of low grade hydrocarbons to engine fuels with the concomitant absorption of large amounts of heat requires high temperature processing in order to overcome the thermodynamic limitations on conversion. Commercial catalytic cracking and reforming catalysts would rapidly deactivate within the order of seconds when applied under the temperatures required to operate an efficient endothermic fuel conversion process.

The overall objective of this research is based on developing a good understanding of the mechanism and theoretical aspects of the behavior of fuels processed by catalysts under supercritical conditions to avoid rapid catalyst deactivation. The approach to be used in this research to gain direct mechanistic information relating to this problem is the use of a novel technique which we developed for examining catalytic reactions via *in-situ* spectroscopic methods under supercritical conditions.

## 3.000 Extended Summary of the Research

### 3.100 *In-Situ* Reaction Monitoring Studies at Supercritical Conditions.

The latest development in our laboratories permits the *in situ* analysis of heterogeneous catalyzed processes by Cylindrical Internal Reflection Infrared Spectroscopy (CIR-FTIR) under autogenous reaction conditions. The technique was developed by Moser et. al. for the *in situ* analysis of homogeneous metal catalyzed reactions and zeolite synthesis under ambient and moderate temperatures and/or high pressures. The advantage of the CIR-IR technique is that it can be used on powders for the *in situ* analysis of a wide variety of chemical reactions when mounted in the appropriate reactor cells. We recently reported that the CIR-FTIR technique demonstrated a definite superiority for *in situ* heterogeneous catalyst analysis. High quality *in situ* spectra was acquired for the first time at temperatures up to 500°C and pressures up to 75 atm permitting direct infrared observation of molecular thermal transition that a hydrocarbon

undergoes in the supercritical regime, the properties of a hydrocarbon within the pores of zeolite (i.e. higher densities than the bulk phase) and *in situ* monitoring the active sites of the catalyst and their interactions with hydrocarbon reactant and products during catalytic cracking at subcritical and supercritical conditions. [See enclosed publication No. 1].

The results showed that the catalyst maintained higher activity when catalytic cracking was performed under the supercritical conditions of the hydrocarbon. On the contrary, the subcritical conditions led to a rapid deactivation of the catalyst. The subcritical IR spectra showed dramatic reductions in the concentration of the acid sites and in the interactions of the acid sites with the olefinic and paraffinic products of the reaction. This was a strong indication of the fact that coke laydown was accelerated in the subcritical regime resulting in a higher degree of active site occupation and therefore, a significant reduction in catalytic activity. However, a lower degree of occupation of the supercages by the solid coke molecules was observed in the supercritical regime. The hydroxyl peaks were intense even after 5 hours of cracking with a significantly higher degree of interactions of the active sites with the olefinic and paraffinic products of the reaction, showing a higher degree of product. Supercritical fuel showed an extraordinary dense behavior within the pores of the zeolite at pressures well into the supercritical regime, which was significantly higher than the estimated values by the equation of states at the same conditions. These results clearly suggest that the super-dense supercritical reaction medium continuously removes coke through solubilization from the zeolite micropores and the external surface, resulting in a partial regeneration of the catalyst formation [See enclosed publication No. 2].

The kinetic analysis by gas chromatography (GC) revealed exactly the same results where the activity loss and selectivity towards coke formation were significantly higher under subcritical conditions. Coke characterization by Thermal Gravimetric Analysis (TGA), and coke chemical analysis at UTRC showed a significantly higher amount of coke present in the catalyst samples that were processed under subcritical conditions. An interesting aspect of the TGA data was that coke that was produced under subcritical conditions burnt at a higher temperature than the catalyst processed under supercritical conditions, showing a higher C/H ratio [see enclosed

publication No. 3]. On the other hand the IR spectra also revealed higher amounts of carbonaceous deposits under subcritical conditions [See enclosed publication No. 2].

The *in situ* CIR-FTIR technique coupled with on line gas chromatography analysis provided a strong experimental proof of the fact that supercritical reaction media can be successfully employed to extract coke-forming compounds from porous catalysts. This eventually results in higher catalytic activities and longer lifetime of the catalyst [See enclosed publications No. 3 & 4]. With this fundamental knowledge, the industry should be able to apply it to improve the process performance since in the current process the catalyst deactivates completely within the order of seconds and requires a continuous regeneration. The regeneration is currently carried out by transferring the coked catalyst to a regeneration unit where coke is burnt off at 650-790°C under oxygen atmosphere and the catalyst restores its original activity.

### **3.200 Chemical Processing within Nanopores under Supercritical Conditions.**

One of the most important discoveries from this research program was that when a supercritical fluid at 475°C was exposed to a variety of nanoporous materials, the density of the fluid within the pores sharply increased at a reduced pressure ( $P/P_c$ ) of 1.2 to densities 1.2 times the density of the liquid within the same micropore at room temperature. The density of the fluid within the pores at this temperature was 15 to 30 times greater than the density of the fluid if it were not contained within the nanoporous material. The maximum reduced density ( $\rho/\rho_L$ ) of 1.4 was observed for Y-type zeolite when the reduced pressure was increased to 2.0. [see enclosed publication No.5]

The above observation is very important to improve the plant productivities and product selectivities of a variety of chemical and petrochemical processes. The chemical reactions that are performed within microporous materials where reactants are held under supercritical conditions during the process will be accelerated in terms of rate of reaction due to the increased concentration of reactants within the nanopores. Catalytic cracking of n-heptane under supercritical heptane conditions using a variety of nanoporous zeolite catalysts demonstrated an increase in the catalytic cracking rate by a factor of 15 compared to the calculated rate in the absence of the



micropore but exposed to the same number of hypothetical active sites. An extension of the WPI observations to more practical endothermic fuels systems was made by a further examination at UTRC in studies on the supercritical conversion of norpar by an H-ZSM-5 catalyst. These results showed a stabilization of the catalyst and a high steady state reactivity. As discussed earlier, these results also showed that the catalytic reaction resulted in a minor deactivation of the catalyst due to a facile removal of coke by the dense supercritical fluid.

### **3.300 *In Situ* CIR-FTIR Studies of the Measurement of Intracrystalline Diffusivities of Hydrocarbons in Zeolites under Supercritical Conditions.**

The CIR-FTIR technique was successfully applied to determine the transport properties of supercritical hydrocarbons within porous catalysts. To our knowledge, this was the first time that the intracrystalline diffusion coefficients of hydrocarbons could be measured under supercritical conditions. Furthermore, these results are important to industrial processes employing porous catalysts at high temperatures, since the CIR-FTIR technique affords a direct measurement of the transport properties of reactants and products under dynamic conditions, typical of industrial applications. [see enclosed publication No. 6]

The results obtained during the self diffusion of n-heptane, counter diffusion of 1-hexene versus n-hexane and co-diffusion of n-heptane/p-xylene mixture in zeolite L under subcritical and supercritical conditions of the hydrocarbons studied showed that the diffusion within the pore was significantly reduced under supercritical conditions (i.e. liquid-like behavior) as the hydrocarbon density within the pore increased.

### **3.400 Mechanism of the Solubilization of Aromatic Hydrocarbons by SCF's**

The *in situ* CIR-FTIR technique developed in our laboratory that employs high temperature/high pressure well-stirred autoclave reactors, enabled the study of the reaction between a wide variety of low molecular weight hydrocarbons under SCF conditions and benzene or polycondensed aromatic hydrocarbon solutes (mainly phenanthrene and 2,3 benzanthracene). This was the first time that the detailed reaction and solubilization mechanisms between hydrocarbon solvents and aromatic molecules (solute) could be observed under supercritical condi-



tions of the hydrocarbons. [See Publication No. 7 and 8]. This technology is potentially important to understanding the mechanism of coal liquefaction by supercritical fluids and other supercritical fluid processing.

The results obtained can be summarized as follows:

The supercritical state substantially altered the C-H bonds in the hydrocarbon molecules, most likely due to enhanced C-H $\cdots$ H-C intermolecular contact interactions.

Reactions of hydrocarbons (paraffins and olefins) with aromatic hydrocarbon compounds that were not expected to take place without the presence of noble metal catalyst, were observed in the supercritical regime. These reactions did not take place at temperatures below the critical point of the principal hydrocarbon component of the mixture.

The aromatic ring(s) for the benzene, phenanthrene and 2,3 benzanthracene molecules was (were) found to be substituted by 2 butane or 1-butene molecules through the addition of a secondary C-H bond in the hydrocarbon molecule.

The reaction rate was higher in the vicinity of the critical point, i.e. at temperatures roughly 10°C above the critical point.

The specific type of C-H bond determined the reactivity of the system. The most effective C-H bond for the reaction with the aromatic ring was a secondary allylic C-H bond followed by a secondary C-H bond.

There was a steric component that inhibits the supercritical reaction.

Reactivity differences in the supercritical regime between different hydrocarbons were determined by the strength of the specific C-H bond, the solvent's ability to stabilize an intermediate carbonium ion involved in the transition state complex and the steric requirements of the hydrocarbon molecule.

#### **4.000 Personnel Supported**

Murat G. Süer (Ph.D. Chemical Engineering, 1996) and Dr. Zissis Dardas (Ph.D. Chemical Engineering, Purdue Univ.)

## 5.000 Enclosed Publications

- [1] Zissis Dardas, Murat G. Süer, Yi H. Ma, and William R. Moser, " *High Temperature, High Pressure In Situ Reaction Monitoring of Heterogeneous Catalytic Processes under Supercritical Conditions by CIR-FTIR* " Journal of Catalysis, **159**, 204-211(1996).
- [2] Murat G. Süer, Zissis Dardas, Yi H. Ma, and William R. Moser, " *An in situ CIR-FTIR Study of n-Heptane Cracking over a Commercial Y-Type Zeolite under Supercritical and Subcritical Conditions* " Journal of Catalysis, **162**, 320-326 (1996).
- [3] Zissis Dardas, Murat G. Süer, Yi H. Ma, and William R. Moser, " *A Kinetic Study of n-Heptane Catalytic Cracking over a Commercial Y-Type Zeolite under Supercritical and Subcritical Conditions* " Journal of Catalysis, **162** 327-338 (1996).
- [4] Murat G. Süer, Zissis Dardas, Yi H. Ma, and William R. Moser, " *Performance of Different Zeolites during n-Heptane Catalytic Cracking under Supercritical Conditions* " Accepted Journal of Catalysis, October 1996.
- [5] Murat G. Süer, Zissis Dardas, Yi H. Ma, and William R. Moser, " *Formation of Super-Dense Phases in Zeolite Micropores under Supercritical Conditions* " prepared to be submitted to Journal of Catalysis, September 1996.
- [6] Murat G. Süer, Zissis Dardas, Yi H. Ma, and William R. Moser, " *An In Situ CIR-FTIR Study of the Diffusion of Hydrocarbons in Zeolites under Supercritical Conditions* " Submitted to AIChE Journal, September 1996.
- [7] Zissis Dardas, Murat G. Süer, Yi H. Ma, and William R. Moser, " *Mechanism of the Solubilization of Aromatic Hydrocarbons by Supercritical Fluids, Part I: An In Situ CIR-FTIR Study of the Reaction of Benzene with Supercritical Butane* " prepared to be submitted to Journal of American Chemical Society, September 1996.
- [8] Zissis Dardas, Murat G. Süer, Yi H. Ma, and William R. Moser, " *Mechanism of the Solubilization of Aromatic Hydrocarbons by Supercritical Fluids, Part II: An In Situ CIR-FTIR Study of the Reaction of Supercritical Hydrocarbon Solvents with Polycondensed Aromatic Compounds* " prepared to be submitted to Journal of American Chemical Society, September 1996.

## 6.000 Interactions/Transitions

### A. Presentations.

Z. Dardas, M.G. Süer, Y.H. Ma, and W.R. Moser, " *An in situ CIR-FTIR Study of the Effect of Supercritical Fluids on Catalyst Stabilization* ", New England Catalysis Society Meeting, Worcester, December 1994.

Z. Dardas, M.G. Süer, Y.H. Ma, and W.R. Moser, " *CIR-FTIR Studies of Supercritical and Subcritical n-Heptane Catalytic Cracking* ", AIChE Summer National Meeting, Boston, August 1995.

W.R. Moser, M.G. Süer, Z. Dardas and Y.H. Ma, " *The Kinetics and Mechanism of Catalytic Cracking under Supercritical Conditions by in situ Cylindrical Internal Reflectance Reactors* " AIChE Spring National Meeting, New Orleans, February 1996.

M.G. Süer, Z. Dardas, W.R. Moser and Y.H. Ma, " *In situ CIR-FTIR Analysis of Hydrocarbon Catalytic Cracking under Supercritical Conditions* " New England Catalysis Society Meeting, Worcester, April 1996.

M.G. Süer, Z. Dardas, W.R. Moser and Y.H. Ma, " *In situ CIR-FTIR and Kinetic Analysis of Hydrocarbon Catalytic Cracking under Supercritical Conditions* " AIChE Annual National Meeting, Chicago, November 1996.

W.R. Moser, M.G. Süer, Z. Dardas and Y.H. Ma, " *Direct Observation of the Molecular Interactions of Supercritical Fluids and their Solutes* " AIChE Annual National Meeting, Chicago, November 1996.

**B. Consultative and Advisory Functions:** None

**C. Transitions:** None

**7.000 New Discoveries, Inventions, or Patent Disclosures :** None

**8.000 Honors/Awards:** Murat G. Süer, Sigma Xi 1995-1996 Doctoral Research Award